International Journal of Luminescence and Applications (ISSN: 2277-6362)
Vol. 5, No. 2, June 2015. Article ID: 096. pp.229-233.

nUV Excitable Red Emitting Eu^{3+} Doped Alkali Earth Silicate Phosphor for Solid State Lighting

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Abstract— *The effect of concentration of Eu^{3+} doped on the photoluminescence properties of $CaMgSiO_4$ is discussed. Interesting behavior, such as the presence of sharp bands centered at 324, 367, 384 and 396nm of Eu^{3+} ion were observed along with CT band centered at 267nm. Among these bands the Eu–O charge transfer band (CTB) is a strong and broad band with FWHM 36nm, and the 396nm sharp band with FWHM 2nm is also stronger one which can be used as excitation source for the generation of white light. This is an interesting multifunctional phosphor. The excitation spectra displayed that this phosphor could be effectively excited by 267nm wavelength so that they could be used as red component for the generation of white light in display and lamp devices and as well the ($^5D_0 \rightarrow {}^7F_1$) 590 and ($^5D_0 \rightarrow {}^7F_2$) 615nm red line becomes the most intense with no other emission lines, could be used as red components for white light-emitting diodes under nUV (396nm) excitation. The results in this work demonstrate that this phosphor is a good candidate luminescent material for use in display and light emitting diodes.*

Keywords— *Photoluminescence, Phosphor, Excitation, Emission, FWHM, nUV*

1. INTRODUCTION

Following an increasing awareness of climate change and environmental issues, people are looking for alternatives to fossil fuels as energy sources that do not emit carbon dioxide [1-3]. White light-emitting diodes (WLEDs) are extensively used and are very important as they significantly reduce global power requirements and the use of fossil fuels [4]. They have attracted substantial attention owing to their extraordinary luminous efficiency, low power consumption, reliability, and environmental friendliness. The quest for phosphors for lighting is one of the most important and urgent challenges to be met by advanced science and high technology, and novel and acceptable fluorescent-material-based solid-state lighting (SSL) must be developed [5]. The intensity, width, durability, and thermal quenching of commercial phosphors for light emitting diodes (LEDs) suggest two exciting approaches of UV-LED chip (with the wavelength of 380-420 nm) and blue-LED chip (with the wavelength of 450-480 nm) for accelerating this development. One involves mixing the emissions from red, green, and blue (RGB) phosphors with a UVLED chip, as in a device with the schematic structure that is shown in the Figure 1.

In recent years, the study on white light phosphors suitable for near-ultraviolet (nUV) excitation has been attracting more attention for fabricating white light emitting diode (LED) with nUV GaN chip for white lighting [6–9]. In comparison with the commercial white LED fabricated with a blue chip and yellow phosphor YAG:Ce^{3+}, the white LED fabricated with nUV chip and corresponding phosphor has higher color stability because all the colors are determined by the phosphors. Up to now, a few white phosphors suitable for nUV excitation have been reported the phosphors with better optical properties are still in development. Rare-earth-ions-doped silicate hosts have demonstrated good photoluminescence properties and chemical–physical stabilities. Eu^{2+} in such kinds of host may emit various colors demanded by white lighting.

Solid-state semiconductor lighting technology can be traced as far back as 1962 to the first semiconductor diode laser announced by Hall [1] at General Electric Research Labs in Schenectady, New York, but there was almost no application besides used in numeric displays or indicator lights in past, because the wavelengths produced by semiconductor lasers have generally been longer than 0.7 μm [10].

However, this situation was completely changed with Shuji Nakamura's invention, who (got Noble Prize in 2015) successfully fabricated double-hetero structure InGaN/GaN blue LED chips for the first time in 1993 and later in 1994 succeeded in producing l-cd-brightness high-power blue InGaN/AlGaN LEDs suitable for commercial

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applications [11−15]. Since the first commercially available white light-emitting diode (LED) was produced by Nichia Corporation in 1996, tremendous progress has been achieved in development of solid-state lighting based on InGaN semiconductors [15, 16]. The operation of LEDs is based on spontaneous light emission in semiconductors, which is due to the radiative recombination of excess electrons and holes that are produced by the injection of current. Therefore, LEDs are not limited by the fundamental factors that still existed in conventional incandescent lamp and compact fluorescent lamp [17]. As a result, LED light sources have superior efficiency, lifetime, reliability, which makes it more energy-saving and environmental-friendly for less thermal radiation and no mercury. The organic light emitting diode (OLED) or polymer light-emitting diode (PLED) has a similar principle of operation with LED, but whose application is restricted by the effect of circumstance on organics.

Here, we focus on LEDs. Currently, the application of LEDs has been extended from signal indicators initially to automobile light, traffic light, street lighting, landscape decoration, backlight of liquid crystal display (LCD) for TV sets, computers and mobile telephones, et al. Converting phosphors are essential components for LEDs. In this paper, we will review the technique of white light generating and the converting phosphors for LEDs to produce idea light with proper luminescence efficiency, color rendering index and thermal stability.

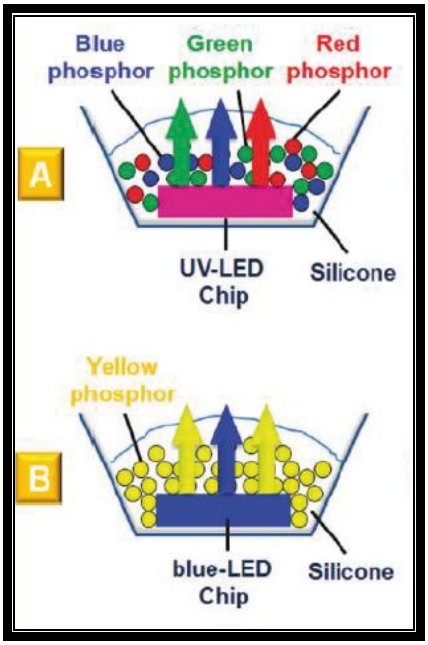

Fig. 1: Schematic structure for the generation of white light

Silicates are good candidates for use in stable host structures because they have high physical-chemical stability, water-resistant properties, stable crystal structures, and excellent optical properties [18, 19].

In this paper, we report luminescent properties of Eu^{3+} doped silicate phosphors with nominal compositions of $2MgCO_3$, $2CaCO_3$, $2SiO_2$, as raw materials for the host and Eu_2O_3 as activator ion. To study the effect of concentration activator ion is doped in the host at 1.5, 2.0, 2.5 and 3.0 mol%.

2. EXPERIMENTAL

2.1 Phosphors Preparation

The phosphors with nominal composition of $2MgCO_3$, $2CaCO_3$, $2SiO_2$ as raw materials for the host and Eu_2O_3 as activator ion were synthesized through a solid-state reaction technique. The samples were doped with 1.5, 2.0, 2.5 and 3.0 mol% of Eu^{3+}. All the above materials were of analytical grade exceeding 99.9% purity. These raw materials in the desired ratio were well milled by an agate mortar and pestle. The mixture is fired at 1300°C for 2 h in air atmosphere

2.2 Characterization

Photoluminescence emission and excitation spectra were measured at room temperature with a Shimadzu RF-5301 PC Spectrofluorophotometer. Xenon lamp was used as excitation source range from 200nm-900nm. The Commission Internationale de l'Eclairage (CIE) coordinates which are calculated using the spectral energy distribution (1931 chart).

3. RESULTS AND DISCUSSION

3.1 Luminescence Study

3.1.1 Excitation and Emission Studies

Fig. 2 shows the PLE spectrum of 1.5, 2.0, 2.5 and 3.0 mol% of Eu^{3+} doped $CaMgSiO_4$ phosphor by monitoring the emission wavelength at 615 nm. The excitation spectrum consists of a strong absorption band between 200–275 nm being centered at 267 nm with FWHM 36 nm, which can be assigned to the Eu–O charge transfer band (CTB). The sharp lines in the wavelength range 275 to 400 nm centered at 324, 367, 387 and 396 nm correspond to f-f transitions ($^7F_0 \rightarrow {}^5H_3$, $^7F_0 \rightarrow {}^5D_0$, $^7F_0 \rightarrow {}^5G_1$, $^7F_0 \rightarrow {}^5L_6$) of Eu^{3+} ion respectively [17, 18]. The absorption intensity of the $^7F_0 \rightarrow {}^5L_6$ transition at 396 nm (FWHM 2nm) is also stronger which is well matching with nUV LED chip is a good sign for pc-LEDs is for the generation of white light.

Fig.3 shows the PL spectra of Eu^{3+} doped at different concentrations in $CaMgSiO_4$ (Eu^{3+} = 1.5, 2.0, 2.5 and 3.0 mol%) under nUV (396nm) excitation wavelength. The PL spectrum exhibited typical emission lines assigned to the transitions $^5D_0$ to ^7F_J (J=1, 2). The intense line at 590 nm is well known to be associated with the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition and the line at 615 nm is corresponds to the electric dipole transition. In this work, the slightly dominant emission peak located at 615 nm are

caused by the electric dipole transition, indicating that the Eu^{3+} ions occupied the sites of non-inversion symmetry [20]. The emission peak of Eu^{3+} at 580 nm originated from the $^5D_0 \rightarrow {}^7F_0$ transition, which is a forbidden transition. The single emission peak at 580 nm indicates that Eu^{3+} occupied only one Mg site.

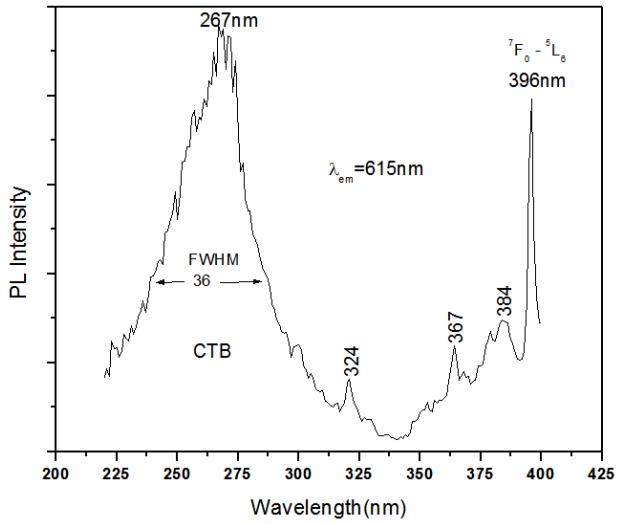

Fig. 2: PLE spectrum of $CaMgSiO_4:Eu^{3+}$ phosphor monitored under 615nm wavelength

From the PL spectra it is observed that the emission intensity is increased with the increase of Eu concentration up to 2.5 mol% and then decreases with the increase of Eu concentration, which indicates that the concentration quenching is taken place.

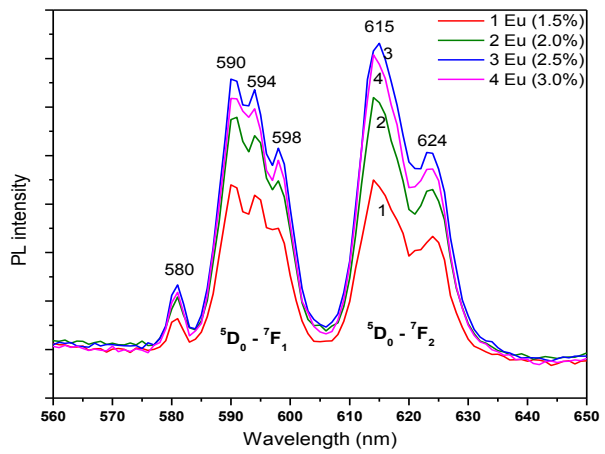

Fig. 3: PL spectrum of $CaMgSiO_4:Eu^{3+}$ (1.5, 2.0, 2.5 & 3.0 mol%) phosphor under 396nm excitation

Fig.4 shows the PL spectra of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor under 267 & 396nm excitations. The emission intensity under 267nm excitation is slightly higher than the emission intensity under 396nm excitation.

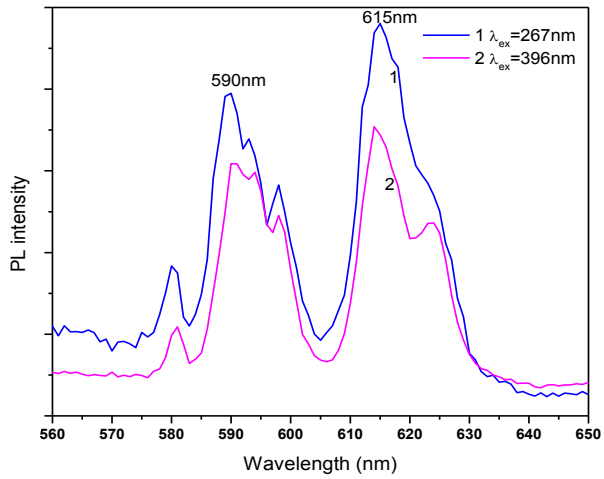

Fig. 4: PL spectrum of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor under 267 & 396nm excitations

3.2 XRD Study

Fig.5 shows the XRD pattern of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor. From the XRD peaks it is observed that the compound mostly in single phase and the dopant did not affect the host structure. The narrow peaks indicate the particle size is in nano meters. The average crystallite size was calculated using Scherrer's formula as 59nm.

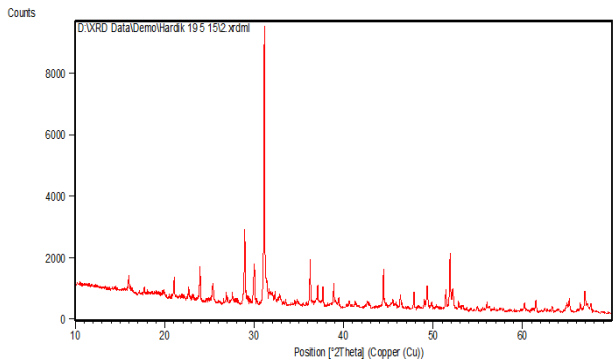

Fig. 5: XRD pattern of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor

Operator	: XPERT
Raw Data Origin	: XRD measurement
Scan Axis	: Gonio
Start Position [°2Th.]	: 9.9942
End Position [°2Th.]	: 69.9942
Step Size [°2Th.]	: 0.0080
Scan Step Time [s]	: 8.2550
Scan Type	: Continuous
PSD Mode	: Scanning
PSD Length [°2Th.]	: 2.12

Divergence Slit Type	: Fixed
Divergence Slit Size [°]	: 0.8709
Specimen Length [mm]	: 10.00
Measurement Temperature [°C]	: 25.00
Anode Material	: Cu
K-Alpha1 [Å]	: 1.54060
Generator Settings	: 40 mA, 45 kV
Goniometer Radius [mm]	: 240.00

3.3 SEM Study

Fig.6 shows the SEM image of the $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor. From the image it is observed that the shape of the particles is irregular and highly agglomerated. The particle size is around 2 – 3 microns.

The emission intensity is low may be due to the large size of the particle.

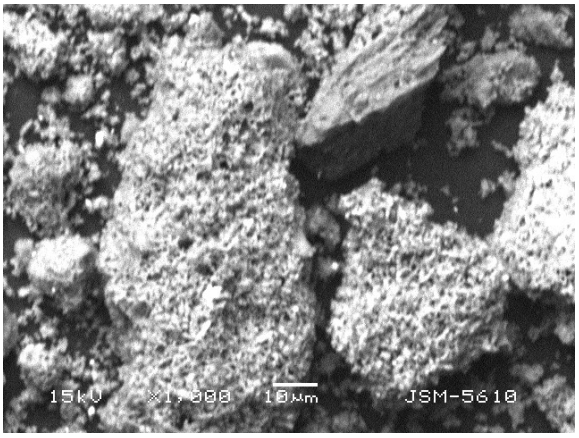

Fig. 6: SEM micrograph of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor

3.4 CIE Coordinates

Fig.7 is the Commission Internationale de l'Eclairage (CIE) coordinates which are calculated using the spectral energy distribution (1931 chart). The CIE co-ordinates of the $CaMgSiO_4:Eu^{3+}$ phosphor are x = 0.608 and y = 0.343. From the CIE co-ordinates the emission colour is in red region within the NTSC modern standard indicating that this can be useful as red component in tri-colour phosphors under nUV excitation for the generation of whitelight.

4. CONCLUSIONS

In summary, $CaMgSiO_4:Eu^{3+}$ phosphors were synthesized successfully via a solid-state reaction. Photoluminescence exhibit a red dominant for luminescence. From XRD studies the compound is mostly in single phase. The chromaticity coordinate of the $CaMgSiO_4:Eu^{3+}$ (2.5 mol %) was found to be (0.608, 0.343) in higher red color purity region. The results in this work demonstrate that this phosphor is expected to be promising candidates for application in display and nUV-WLEDs.

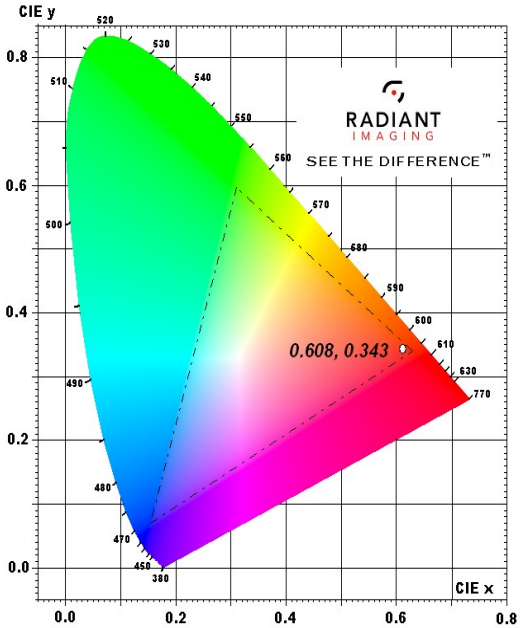

Fig. 7: CIE co-ordinates of $CaMgSiO_4:Eu^{3+}$ (2.5 mol%) phosphor depict on 1931 chart

ACKNOWLEDGEMENTS

The author is gratefully thanking University Grant Commission (UGC), New Delhi, India for providing financial support under Minor research Project (MRP).

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